

# Coherent Phase Control in Closed and Open Quantum Systems: A General Master Equation Approach

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The underlying mechanisms for one photon phase control are revealed through a master equation approach. Specifically, two mechanisms are identified, one operating on the laser time scale and the other on the time scale of the system-bath interaction. The effect of the secular and non-secular Markovian approximations are carefully examined.

## 1 Introduction:

The possibility of manipulating and controlling quantum systems by using quantum features is the goal of many modern control protocol<sup>1</sup>. An unusual type of control, one photon phase control (OPPC), has been the subject of recent attention and discussion (see, e.g., Faraday Discussions 153<sup>2</sup>). In this case, control takes place by varying the relative *phase* of components of a weak pulse, while keeping the power spectrum of the light source fixed. A seminal proof<sup>3</sup> showed that one-photon phase control was not possible for isolated molecular systems in which control is over products in the continuum. A subsequent experiment on control of retinal isomerization in bacteriorhodopsin<sup>4</sup> motivated controversy<sup>5-8</sup> and the need for clarification of conditions under which such control was possible. This clarification, provided in Ref. 9 showed that control was *possible* for both closed systems and for open quantum systems under well defined conditions. Specifically, we showed the following for control of an observable  $\hat{O}$  in a system defined by Hamiltonian  $\hat{H}_M$ :

(a) If the system is closed (i.e., not coupled to an environment), then one-photon phase control is possible if  $[\hat{H}_M, \hat{O}] \neq 0$ . For example, control over isomerization in an isolated molecule is possible since the probability of observing an isomer (e.g., *cis* or *trans*) is an observable that does not commute with  $\hat{H}_M$ .

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The situation is similar for control over product formation in radiationless transitions, such as intersystem crossing and internal conversion<sup>10</sup>.

However, if  $[\hat{H}_M, \hat{O}] = 0$ , then one-photon phase control is not possible in an isolated system.

(b) If the system is coupled to an environment then, as above, control is possible if  $[\hat{H}_M, \hat{O}] \neq 0$ . However, even in the case where  $[\hat{H}_M, \hat{O}] = 0$  control may still be possible, in which case it is *environmentally assisted*.

Reference 9 provided these general rules, derived in a somewhat different way below, but did not provide any insight into the way in which environmental assistance works, or the conditions under which such control is appreciable. This is the subject of this paper. Specifically, we demonstrate the significant role of non-Markovian dynamics and strong system-bath coupling in enhancing the extent of one-photon phase control. To do so we utilize a master equation based approach to the open system case, which, as seen below, proves enlightening. The net result of this paper is the demonstration of the underlying mechanism responsible for environmentally assisted one-photon phase control.

Note, also, as an aside, that we have also computationally demonstrated<sup>11</sup> one-photon phase control in a model retinal system, making a connection with the original experiments on related systems.

## 2 One-photon phase control and closed quantum systems.

Let us consider a molecular system M described by the Hamiltonian  $\hat{H}_M$  with  $\hat{H}_M|a\rangle = E_a|a\rangle$ . If the system state is described by the density operator  $\hat{\rho}_M$ , the expectation value of a given observable  $\hat{O}$  of system M at time  $t$  can be calculated as

$$\langle \hat{O}(t) \rangle = \sum_{a,b} \langle a | \hat{O} | b \rangle \langle b | \hat{\rho}_M | a \rangle. \quad (1)$$

If  $[\hat{H}_M, \hat{O}] = 0$ , we simply get

$$\langle \hat{O}(t) \rangle = \sum_a \langle a | \hat{O} | a \rangle \langle a | \hat{\rho}_M | a \rangle. \quad (2)$$

For this case, only diagonal terms contribute to the time evolution of the expectation value of the observable  $\hat{O}$ .

The essence of phase control is trying to manipulate the expectation of  $\hat{O}$  by changing the *phase* of an applied laser pulse. When the laser pulse is taking into account, the Hamiltonian can be re-written as  $\hat{H}_0 = \hat{H}_M + \hat{H}^{\text{MR}} = \hat{H}_M - \hat{\mathbf{d}} \cdot \mathbf{E}(z, t)$ , with  $\mathbf{E}(z, t) = \mathcal{E}\mathcal{E}(z, t)$  where

$$\mathcal{E}(z, t) = \int_{-\infty}^{\infty} d\omega \epsilon(\omega) \exp \left[ -i\omega \left( t - \frac{z}{c} \right) \right], \quad (3)$$

is the amplitude of the field with polarization vector  $\mathcal{E}$ , which can be expressed in terms of frequency spectrum  $\epsilon(\omega) = |\epsilon(\omega)| \exp(i\phi[\omega])$  and,  $\hat{\mathbf{d}}$  is the transition-dipolar operator. We are interested in manipulating the time evolution of the observable  $\hat{O}$  by means of varying the spectral phase  $\phi(\omega)$  only.

In order to clearly understand the role of the environment in OPPC, it is illustrative to analyze in detail the circumstances under which<sup>9</sup> phase control is

not possible. The evolution of the density matrix, for unitary time-evolution, is governed by

$$\dot{\rho}_{ab} = -i\omega_{ab}\rho_{ab} + \frac{i}{\hbar} \sum_c [H_{ac}^{\text{MR}}(t)\rho_{cb} - \rho_{ac}H_{cb}^{\text{MR}}(t)] \quad (4)$$

where  $\rho_{ab} = \langle a|\hat{\rho}_{\text{M}}|b\rangle$ ,  $\hbar\omega_{ab} = E_a - E_b$  and  $H_{ab}^{\text{MR}}(t) = d_{ab}\mathcal{E}(z,t) = \langle a|\hat{\epsilon} \cdot \hat{\mathbf{d}}|b\rangle \mathcal{E}(z,t)$ . Due the unitary character of the dynamics, we can integrate Eq. (4) out by means of a the following ansatz for the wavefunction

$$|\Psi\rangle = \sum_n b_n(t)|E_n\rangle \exp\left(-\frac{i}{\hbar}E_n t\right), \quad (5)$$

with  $\hat{\rho}_{\text{M}}(t) = |\Psi(t)\rangle\langle\Psi(t)|$ .

Let us consider, e.g., that the molecule is initially ( $t = -\infty$ ) in the pure state  $|E_1\rangle$ , so we have  $b_1(t = -\infty) = 1$  and  $b_k(t = -\infty) = 0$  for  $k \neq 1$ . After formally integrating Eq. (5) for  $b_m$ , we get

$$b_m(t) = \int_{-\infty}^t ds b_1(s) \exp(i\omega_{m,1}s) H_{m1}^{\text{MR}}(s). \quad (6)$$

If the perturbation is weak, for unitary evolution, one can assume that  $b_1(t) = 1$  at all times, thus

$$b_m(t) = \frac{i}{\hbar} d_{m1} \int_{-\infty}^{\infty} d\omega \bar{\epsilon}(\omega) \int_{-\infty}^t ds \exp(i(\omega_{m,1} - \omega)s), \quad (7)$$

where we have made use of Eq. (3) and defined  $\bar{\epsilon}(\omega) = \epsilon(\omega) \exp(i\omega z/c)$ . Since our interest is in the long time regime, we extend the upper integration limit to infinity and get  $2\pi\delta(\omega_{m1} - \omega)$  for the integral over  $s$ . Finally, we have

$$b_m(\infty) = 2\pi \frac{i}{\hbar} d_{m1} |\epsilon(\omega_{m1})| \exp\left[i\left(\phi(\omega_{m1}) + \frac{1}{c}\omega_{m1}z\right)\right], \quad (8)$$

which yields

$$\begin{aligned} \rho_{ab}(t) &= \frac{4\pi}{\hbar^2} d_{a1} d_{b1}^* |\epsilon(\omega_{a1})| |\epsilon(\omega_{b1})| \exp(-i\omega_{ab}t) \\ &\times \exp\left\{i\left[\phi(\omega_{a1}) - \phi(\omega_{b1}) + \frac{z}{c}(\omega_{a1} - \omega_{b1})\right]\right\}. \end{aligned} \quad (9)$$

From here, it is clear that no spectral phase information is present in the diagonal terms,  $a = b$ , and therefore it is impossible to manipulate the time evolution of the observable  $\hat{O}$  in Eq. (2).

Based on the equation (9), it is easy to track the vanishing of the spectral phase contribution to the fact that  $\hat{\rho}_{\text{M}}$  was constructed as the projector onto the state  $|\Psi(t)\rangle$ , i.e., to the fact that the evolution is unitary. This can be understood as follows. Under unitary time evolution, the dynamics is generated by the unitary time-evolution operator  $\hat{U}(t) = \hat{T} \exp(-i \int_{t_0}^t ds \hat{H}(s)/\hbar)$ , by means of the relation  $\hat{\rho}_{\text{M}}(t) = \hat{U}(t)\hat{\rho}_{\text{M}}(0)\hat{U}^\dagger(t)$ . If  $\hat{\rho}(0)$  represents the density operator of a pure state  $|\Psi\rangle$ , then  $\hat{U}(t)$  evolves  $|\Psi\rangle$  (in the direct Hilbert space) while  $\hat{U}^\dagger(t)$  evolves  $\langle\Psi|$

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(in the dual Hilbert space). Since the generator in the dual space,  $\hat{U}^\dagger(t)$ , is just the time-reversed version of the generator in the direct space,  $\hat{U}(t)$ , then the evolution in the two spaces interfere in the density operator in such a way that no phase information is encoded in the diagonal elements [see Eq. (9)]. This will no longer be true in the case of non-unitary dynamics (e.g., for open quantum systems) because of the time-symmetry breaking. This fact can be identified as a first contribution from the environment to OPPC (see below).

In what follows, we explore in detail the possible ways in which the environment can support the generation of OPPC.

### 3 One-photon phase control and open quantum systems.

The study of open-quantum-systems dynamics is a demanding and intricate task due to the various time/energy and coupling strength scales involved. In the case of molecular systems, it is common that one component of the system plays the role of the environment. For example, if one is interested in the electronic dynamics, then the vibrational and rotational modes of the same system comprise the environment. In this situation, one expects that the coupling to the environment is strong and the dynamics are non-local in time, i.e., it depends on the previous conformational states of the molecular system (non-Markovian dynamics)<sup>12</sup>. This non-local character of the dynamics has been proved to be vital in physical systems under the influence of external fields<sup>13,14</sup>. Additionally, there is no apparent justification for neglecting the initial correlations between the part we name the system and the part we name the environment. All these features prevent us from applying standard approximation schemes and somehow hide the underlying physical processes.

In order to identify the contribution from the environment to the one-photon phase control, we consider the following situation: a molecular system  $M$  is at equilibrium with its environment, a stationary/incoherent situation that is subsequently irradiated by a coherent laser pulse. In the first part of our analysis, Sec. (3.1), we neglect the initial correlation between the system and the environment and discuss how the non-unitary dynamics induced by the environment could assist OPPC. In the second part, Sec. (3.2), we include the initial correlations with the environment and show how they could enhance the role of the environment in assisting OPPC.

#### 3.1 Influence of the non-unitary dynamics

In order to consider the influence of the environment on the system in a consistent way, we start by considering the total dynamics of the two parts by means of the total Hamiltonian

$$\hat{H} = \hat{H}_M + \hat{H}^{\text{ME}} + \hat{H}_E + \hat{H}^{\text{MR}}, \quad (10)$$

where  $\hat{H}^{\text{ME}}$  denotes the interaction between the system and the environment and  $\hat{H}_E$  characterizes the environment. Let us consider that the interaction between the system and the bath is of the general form

$$\hat{H}^{\text{ME}} = \sum_u \hat{K}_u \otimes \hat{\Phi}_u, \quad (11)$$

where  $\hat{K}_u$  and  $\hat{\Phi}_u$  are operators of the system and the environment, respectively. Note that  $\hat{K}_u$  and  $\hat{\Phi}_u$  could be non-Hermitian as long as  $\hat{H}^{\text{ME}}$  is Hermitian. At this point we assume that the initial density operator  $\hat{\rho}_{\text{ME}}$  of the system+bath factorizes at  $t = t_0$  into a product of the system part  $\hat{\rho}_{\text{M}}$  and the environment part  $\hat{\rho}_{\text{E}}$ , that is as  $\hat{\rho}_{\text{ME}}(t_0) = \hat{\rho}_{\text{M}}(t_0) \otimes \hat{\rho}_{\text{E}}(t_0)$ .

For this case, the non-Markovian evolution of the system density matrix elements can be cast in the form (cf. Chapter 3 in Ref. 15)

$$\begin{aligned} \dot{\rho}_{ab} = & -i\omega_{ab}\rho_{ab} + \frac{i}{\hbar} \sum_c (H_{ac}^{\text{MR}}\rho_{cb} - \rho_{ac}H_{cb}^{\text{MR}}) \\ & - \sum_{c,d} \int_0^{t-t_0} d\tau \left\{ M_{cd,db}(-\tau)e^{i\omega_{da}\tau}\rho_{ac}(t-\tau) + M_{ac,cd}(\tau)e^{i\omega_{bc}\tau}\rho_{db}(t-\tau) \right. \\ & \left. - \left[ M_{db,ac}(-\tau)e^{i\omega_{bc}\tau} + M_{db,ac}(\tau)e^{i\omega_{da}\tau} \right] \rho_{cd}(t-\tau) \right\}, \end{aligned} \quad (12)$$

where  $M_{ab,cd}(t)$  determines the time span for correlations and are called the memory matrix elements (cf. Chapter 3 in Ref. 15). They are defined by

$$M_{ab,cd}(t) = \sum_{u,v} C_{uv}(t) K_{ab}^{(u)} K_{cd}^{(v)}, \quad (13)$$

and satisfy the relation  $M_{ab,cd}^*(t) = M_{dc,ba}(-t)$ . The reservoir correlation function  $C_{uv}(t)$  is given by

$$C_{uv}(t) = \frac{1}{\hbar^2} \langle \Phi_u(t) \Phi_v(0) \rangle_{\text{R}} - \frac{1}{\hbar^2} \langle \Phi_u \rangle_{\text{R}} \langle \Phi_v \rangle_{\text{R}}, \quad (14)$$

where  $\langle \Phi_u(t) \Phi_v(0) \rangle_{\text{R}} = \text{tr}[\hat{\rho}_{\text{E,eq}} \Phi_u(t) \Phi_v(0)]$ . The first line in Eq. (12) describes the unitary evolution and is completely equivalent to Eq. (4). Hence, if no phase control can be achieved from Eq. (4), no phase control can be achieved from this part of the evolution in Eq. (12). The remaining lines describe the non-unitary non-Markovian dynamics, characterized by the non-local evolution implied by the integration from 0 to  $t - t_0$ . The most relevant feature of this second part of Eq. (12) is the fact that the off-diagonal elements affect the dynamics of the diagonal terms, despite the weak field condition.

Consider then the case where the system is initially in equilibrium with the bath and the excitation follows. If we write Eq. (12) as  $\dot{\hat{\rho}}_{\text{M}} = -i\hat{\mathcal{L}}\hat{\rho}_{\text{M}} - \hat{\mathcal{D}}\hat{\rho}_{\text{M}} - i\hat{\mathcal{L}}_{\text{laser}}\hat{\rho}_{\text{M}}$ , then our initial state is an eigenstate of the super operator  $\hat{\mathcal{T}} \exp[-i \int_{t_0}^t ds (\hat{\mathcal{L}}(s) - i\hat{\mathcal{D}}(s))]$ , i.e.,  $\hat{\mathcal{T}} \exp[-i \int_{t_0}^t ds (\hat{\mathcal{L}}(s) - i\hat{\mathcal{D}}(s))] \hat{\rho}_{\text{M}} = \lambda_{\hat{\rho}_{\text{M}}} \hat{\rho}_{\text{M}}$ . Here  $\hat{\mathcal{L}}$  comprises the contribution from the system Hamiltonian  $H_{\text{M}}$  while  $\hat{\mathcal{D}}$  provides for the effect of the bath on the system and  $\hat{\mathcal{L}}_{\text{laser}}$  accounts for the action of the laser pulse. For high enough temperature and weak coupling to the bath [cf. Ref. 16 and reference therein], one can show that in the long time regime, and in the absence of the laser, the density operator of the system is (where  $|n\rangle$  are eigenstates of  $H_{\text{M}}$ ).

$$\hat{\rho}_{\text{M,can}} = \lim_{t \rightarrow \infty} \hat{\rho}_{\text{M}}(t) = \frac{1}{Z} e^{-\hat{H}_{\text{M}}\beta} = \frac{1}{Z} \sum_n e^{-E_n\beta} |n\rangle \langle n|, \quad (15)$$

Here  $Z$  is the partition function  $Z = \text{tr}(e^{-\hat{H}_{\text{M}}\beta})$  and  $\beta = 1/k_{\text{B}}T$ , is an eigenstate of non-driven dynamics with eigenvalue 1, i.e.,  $\exp[-i \int_{t_0}^t ds (\hat{\mathcal{L}}(s) - i\hat{\mathcal{D}}(s))] \hat{\rho}_{\text{M,can}} =$

$\hat{\rho}_{M,\text{can}}$  or equivalently,  $\hat{\rho}_{M,\text{can}}$  is a zero mode of the generator  $\hat{\mathcal{L}}(s) - i\hat{\mathcal{D}}(s)$ . Thus, in this description the laser excitation finds the system in an incoherent superposition of energy eigenstates.

For this initial state, under the weak field assumption, we can solve Eq. (12) perturbatively in the laser term,

$$\dot{\hat{\rho}}_M^{(0)}(t) = -i(\hat{\mathcal{L}} - i\hat{\mathcal{D}})\hat{\rho}_{M,\text{can}}, \quad (16)$$

$$\dot{\hat{\rho}}_M^{(1)}(t) = -i(\hat{\mathcal{L}} - i\hat{\mathcal{D}})\hat{\rho}_M^{(0)}(t) - i\hat{\mathcal{L}}_{\text{laser}}\hat{\rho}_M^{(0)}(t), \quad (17)$$

$$\dot{\hat{\rho}}_M^{(2)}(t) = -i(\hat{\mathcal{L}} - i\hat{\mathcal{D}})\hat{\rho}_M^{(1)}(t) - i\hat{\mathcal{L}}_{\text{laser}}\hat{\rho}_M^{(1)}(t). \quad (18)$$

The zeroth-order term  $\hat{\rho}_M^{(0)}(t)$  describes the dynamics in the absence of the laser and based on the description above, can be trivially obtained as  $\hat{\rho}_M^{(0)}(t) = \hat{\rho}_{M,\text{can}}$ . The first-order term  $\hat{\rho}_M^{(1)}(t)$  accounts for the dynamics induced by the laser pulse on the incoherent superposition of eigenstates  $\hat{\rho}_{M,\text{can}}$ . Since  $-i(\hat{\mathcal{L}} - i\hat{\mathcal{D}})\hat{\rho}_M^{(0)}(t) = -i(\hat{\mathcal{L}} - i\hat{\mathcal{D}})\hat{\rho}_{M,\text{can}} = 0$ , the system-bath contribution is absent here.

In deriving Eq. (9), we had assumed that  $\hat{\rho}_M(0) = |1\rangle\langle 1|$ , whereas in our case we have an incoherent superposition of eigenstates (15). Hence, by virtue of the linearity of the master equation (12), we can infer directly that

$$\begin{aligned} \rho_{ab}^{(1)}(t) &= \frac{1}{Z} \frac{4\pi}{\hbar^2} \sum_n e^{-E_n\beta} d_{an} d_{bn}^* |\epsilon(\omega_{an})| |\epsilon(\omega_{bn})| \exp(-i\omega_{ab}t) \\ &\times \exp\left\{i\left[\phi(\omega_{an}) - \phi(\omega_{bn}) + \frac{z}{c}(\omega_{an} - \omega_{bn})\right]\right\}. \end{aligned} \quad (19)$$

Therefore, it is clear that from Eq. (19) that no phase information is encoded in the populations,  $a = b$ , of  $\hat{\rho}_M^{(1)}(t)$ .

The second-order term  $\hat{\rho}_M^{(2)}(t)$  accounts for the evolution of the state prepared by the laser excitation in the presence of the system-bath dynamics. For the populations of  $\hat{\rho}_M^{(2)}$  we have

$$\begin{aligned} \dot{\rho}_{aa}^{(2)} &= \frac{i}{\hbar} \sum_c \left( H_{ac}^{\text{MR}} \rho_{ca}^{(1)} - \rho_{ac}^{(1)} H_{ca}^{\text{MR}} \right) \\ &- \sum_{c,d} \int_0^{t-t_0} d\tau \left\{ M_{cd,da}(-\tau) e^{i\omega_{da}\tau} \rho_{ac}^{(1)}(t-\tau) + M_{ac,cd}(\tau) e^{i\omega_{ac}\tau} \rho_{da}^{(1)}(t-\tau) \right. \\ &\left. - \left[ M_{da,ac}(-\tau) e^{i\omega_{ac}\tau} + M_{da,ac}(\tau) e^{i\omega_{da}\tau} \right] \rho_{cd}^{(1)}(t-\tau) \right\}, \end{aligned} \quad (20)$$

Explicitly integrating Eq. (20) requires that we specify the system-bath interactions [Eq. (11)] and the bath nature. For real environments this integration is not possible and one has to appeal to specific models; in the Appendix we discuss the most relevant features of the commonly used bosonic bath. Despite the sheer complexity of integrating Eq. (20), one can still extract some of the relevant physical contributions directly from the master equation (as an example, see Ref. 17 for a specific implementation). By inserting Eq. (19) into the right-hand side of Eq. (20), it is clear that phase control of the population will result from the system-bath interaction, which couples  $\rho_{ab}^{(1)}$  to  $\rho_{aa}^{(2)}$ . This phase control is of

second order in both the radiation field and in the system-bath coupling strength. Note that the radiation field (the first two terms) also couples  $\rho_{ab}^{(1)}$  to  $\rho_{aa}^{(2)}$ . This contribution, however, is third order in the radiation field and thus is negligible in our current considerations of second order effects.

The time dependence of the M matrix elements signifies the non-Markovian character of the dynamics, which can be associated with the environment self-correlations. These self-correlations allows for a back and forth information flow between the system and the bath<sup>18</sup>. If the dynamics is Markovian (see next case below), the information flow is unidirectional: from the system to the bath. This information flow can be understood as an entropy flux and in the case of Markovian dynamics results in an always increasing entropy of the system M. In the presence of external driving fields, non-Markovian terms are essential<sup>19</sup>. In our case, this back and forth flow allows for an *efficient* transfer of phase information via the bath. Additionally, the non-Markovian dynamics is characterized by slower correlations decay-rate<sup>20</sup>, allowing thus the presence of phase control for longer times<sup>17</sup>.

**3.1.1 Markovian Approximation**—If the environment quickly “forgets” any internal self-correlations during its interaction with the system, that is, if any dynamically established quantum correlations between parts of the environment are destroyed on a time scale much shorter than the characteristic time scale of the interaction-picture reduced density operator of the system, the Markovian approximation can be invoked. Mathematically, this means that the correlations  $C_{uv}(\tau)$ , and hence the M matrix elements, die off quickly as  $\tau > 0$ , and thus the  $\tau$  integral in Eq. (20) picks up contribution only from  $\rho_{ab}^{(1)}(t)$ , rendering the dynamics time-local. Moreover, it does not make a difference if we extend the upper limit of integration to infinity, in which case the matrix elements  $\Gamma_{ab,cd}$ , defined below, become constant. As a result, a Markovian master equation is obtained:

$$\begin{aligned} \dot{\rho}_{aa}^{(2)} = & \frac{i}{\hbar} \sum_c \left( H_{ac}^{\text{MR}} \rho_{ca}^{(1)} - \rho_{ac}^{(1)} H_{ca}^{\text{MR}} \right) \\ & - \sum_{c,d} \left\{ \Gamma_{ad,dc}(\omega_{cd}) \rho_{ac}^{(1)}(t) + \Gamma_{ac,cd}(\omega_{dc}) \rho_{da}^{(1)}(t) \right. \\ & \left. - [\Gamma_{ca,ad}(\omega_{da}) + \Gamma_{da,ac}(\omega_{ca})] \rho_{cd}^{(1)}(t) \right\}, \end{aligned} \quad (21)$$

where

$$\Gamma_{ab,cd}(\omega) = \Re \int_0^\infty d\tau e^{i\omega\tau} M_{ab,cd}(\tau) = \Re \sum_{u,v} K_{ab}^{(u)} K_{cd}^{(v)} \int_0^\infty d\tau e^{i\omega\tau} C_{uv}(\tau). \quad (22)$$

This master equation retains the essential feature of the coupling of  $\rho_{ab}^{(1)}$  to  $\rho_{aa}^{(2)}$  as in Eq. (20). *As a result, even given the Markovian approximation, the population will show phase dependence of second order in the radiation field and of second order in the system-bath coupling.* The Markovian approximation, which results in the time locality of the master equation, does not undermine the essential feature of phase dependence in the population. However, Markovian dynamics results, in general, in a stronger correlations decay-rate<sup>20</sup> and therefore, the phase information will rapidly flow back to the bath. *Hence, phase control may not be noticeable when the bath relaxation is very fast.*



**3.1.2 Markovian Secular Approximation**—If, in addition, one now applies the secular approximation in Eq. (21), we get

$$\begin{aligned}\dot{\rho}_{aa}^{(2)} = & \frac{i}{\hbar} \sum_c \left( H_{ac}^{\text{MR}} \rho_{ca}^{(1)} - \rho_{ac}^{(1)} H_{ca}^{\text{MR}} \right) \\ & - 2 \sum_c \left[ \Gamma_{ac,ca}(\omega_{ac}) \rho_{aa}^{(1)}(t) - \Gamma_{ca,ac}(\omega_{ca}) \rho_{cc}^{(1)}(t) \right].\end{aligned}\quad (23)$$

This approximation decouples the evolution of the diagonal elements from that of the off-diagonal terms via the bath. Hence no phase control in the population can be observed, due to the artificial truncation of the off-diagonal terms. Thus, the secular approximation is not appropriate for the study of environmentally assisted phase control. *Alternatively, from a physics perspective, if the secular approximation is indeed valid for some system of interest, then our analysis shows that OPPC is not achievable in such a system.*

### 3.2 The significant influence of the initial system-bath correlations

The presence of initial correlations between the system and bath,  $\hat{\rho}_{\text{ME}}(t_0) \neq \hat{\rho}_{\text{M}}(t_0) \otimes \hat{\rho}_{\text{E}}(t_0)$ , introduces an important new contribution in the master equation [Eq. (12)]. For completeness we write the entire expression,

$$\begin{aligned}\dot{\rho}_{ab} = & -i\omega_{ab}\rho_{ab} + \frac{i}{\hbar} \sum_c \left( H_{ac}^{\text{MR}} \rho_{cb} - \rho_{ac} H_{cb}^{\text{MR}} \right) \\ & - \frac{i}{\hbar} \sum_u \langle a | \text{tr}_{\text{E}} \left( [\hat{K}_u \hat{\Phi}_u, \hat{\rho}_{\text{ME}}(t_0)] - [\hat{K}_u \hat{\Phi}_u, \hat{\rho}_{\text{E}}(t_0) \hat{\rho}_{\text{M}}(t_0)] \right) | b \rangle \\ & - \sum_{c,d} \int_0^{t-t_0} d\tau \left\{ M_{cd,db}(-\tau) e^{i\omega_{da}\tau} \rho_{ac}(t-\tau) + M_{ac,cd}(-\tau) e^{i\omega_{bc}\tau} \rho_{db}(t-\tau) \right. \\ & \left. - [M_{db,ac}(-\tau) e^{i\omega_{bc}\tau} + M_{db,ac}(-\tau) e^{i\omega_{da}\tau}] \rho_{cd}(t-\tau) \right\},\end{aligned}\quad (24)$$

where  $\hat{\rho}_{\text{E}}(t_0) = \text{tr}_{\text{S}} \hat{\rho}_{\text{ME}}(t_0)$  and  $\hat{\rho}_{\text{M}}(t_0) = \text{tr}_{\text{E}} \hat{\rho}_{\text{ME}}(t_0)$ . The new term in the dynamics exposes the initial correlations between the system and the environment. Note that this is an extension beyond standard master equations, which do not usually include the state of the environment explicitly.

If  $\hat{\rho}_{\text{ME}}(t_0)$  factorizes into system and bath terms, then it is clear that the terms in the second line in Eq. (24), the ones which account for the initial correlations, vanish. In the opposite case, this would imply that the initial stationary state should be re-derived taking into account this new driving term, i.e., the new stationary state will not be diagonal in the energy eigenbasis. The immediate consequence of this fact is that the initial state, before the coherent excitation takes place, will contain stationary coherences<sup>14</sup>, i.e. non-zero time independent off-diagonal elements of the system density matrix in the energy representation, which will allow for phase control.

As in the previous case, we can write Eq. (24) as  $\dot{\hat{\rho}}_{\text{M}} = -i\hat{\mathcal{L}}\hat{\rho}_{\text{M}} - i\hat{\mathcal{L}}_0\hat{\rho}_{\text{M}} - \hat{\mathcal{D}}\hat{\rho}_{\text{M}} - i\hat{\mathcal{L}}_{\text{laser}}\hat{\rho}_{\text{M}}$  and assume that the initial state is an eigenstate of the superoperator  $\hat{\mathcal{T}} \exp[-i \int_{t_0}^t ds (\hat{\mathcal{L}}(s) + \hat{\mathcal{L}}_0(s) - i\hat{\mathcal{D}}(s))]$ . Here  $\hat{\mathcal{L}}$ ,  $\hat{\mathcal{D}}$ ,  $\hat{\mathcal{L}}_{\text{laser}}$  are defined as before and  $\hat{\mathcal{L}}_0$  denotes the contribution from the initial correlations given in the



second line of Eq. (24). Due to the initial correlations between the system and the bath, it is clear that in the eigenstates of the super operator  $\hat{\mathcal{T}} \exp[-i \int_{t_0}^t ds (\hat{\mathcal{L}}(s) + \hat{\mathcal{L}}_0(s) - i\hat{\mathcal{D}}(s))]$  are no longer diagonal in the eigenbasis of  $\hat{H}_M$ . For this case,

$$\hat{\rho}_{M,\text{eq}} = \lim_{t \rightarrow \infty} \hat{\rho}_M(t) = \frac{1}{Z'} \text{tr}_E e^{-(\hat{H}_M + \hat{H}^{\text{ME}} + \hat{H}_E)\beta}, \quad (25)$$

where  $Z' = \text{tr}(e^{-(\hat{H}_M + \hat{H}^{\text{ME}} + \hat{H}_E)\beta})$  is the partition function. Thus, in this case the laser excitation finds the system with stationary coherences of energy eigenstates, a concept that we have discussed in Ref. 14. *The presence of these off-diagonal elements guarantees that the phases of the laser pulse contribute to the dynamics of the populations.*

Following a perturbative approach similar to that in Sec. 3.1, we can study the dynamics by means of the sequence

$$\dot{\hat{\rho}}_M^{(0)}(t) = -i(\hat{\mathcal{L}} + \hat{\mathcal{L}}_0 - i\hat{\mathcal{D}})\hat{\rho}_{M,\text{eq}}, \quad (26)$$

$$\dot{\hat{\rho}}_M^{(1)}(t) = -i(\hat{\mathcal{L}} + \hat{\mathcal{L}}_0 - i\hat{\mathcal{D}})\hat{\rho}_M^{(0)}(t) - i\hat{\mathcal{L}}_{\text{laser}}\hat{\rho}_M^{(0)}(t), \quad (27)$$

$$\dot{\hat{\rho}}_M^{(2)}(t) = -i(\hat{\mathcal{L}} + \hat{\mathcal{L}}_0 - i\hat{\mathcal{D}})\hat{\rho}_M^{(1)}(t) - i\hat{\mathcal{L}}_{\text{laser}}\hat{\rho}_M^{(1)}(t), \quad (28)$$

Since the off-diagonal elements in the system energy eigenbasis are present from the beginning, phase control of the population will take place at the time scale of the radiation field. In other words, the phase information can “flow” directly into the population via the radiation, without having to wait for the system-bath interaction to first establish phase dependence in the off-diagonal elements.

## 4 Concluding Remarks

Environmentally assisted one-photon phase control arises in open systems when control is achieved over system properties that commute with the system Hamiltonian. In such cases, phase control is not possible unless the environment participates in the dynamics. In this paper we have analyzed the origins of such control and shown that the effects of molecule-bath coupling on phase control are two-fold and take place on two different time scales. First, the thermalization of the coupled system-bath gives rise to non-zero off-diagonal elements in the initial molecular state, which can result in a direct phase control of the population; this control takes place at the timescale of the radiation field. Second, through the molecule-bath coupled dynamics, as modeled by Eq. (20) or Eq. (21), the phase information contained in the off-diagonals can “flow” through the bath into the diagonal elements, resulting in an indirect phase control; this control takes place on the timescale of the molecule-bath interaction. The different timescales provide useful indicators to distinguish the two kinds of phase control in experiments.

One final note is in order. Environmentally assisted one-photon phase control depends on the system-bath interaction. In the case where the bath is in equilibrium this interaction will cause, long after the pulse is over, the system to relax to a laser-phase-independent equilibrium state as well. As such, and under these circumstances, environmentally assisted one-photon phase control will only survive for a well defined time after the laser excitation is over. Rates and time scales over which this control persists is dependent upon, and requires numerical studies of, individual systems of interest.

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## Appendix: Harmonic Oscillator Bath

Since the explicit calculation of the correlation functions  $C_{uv}$  in Eq. (14) is not feasible for real baths such as solvents, one has to appeal to specific models of the bath and the system-bath interaction. The most common approximation is the normal mode approximation. In this case one assumes that, e.g., the vibrational modes can be described by small oscillations around the equilibrium point, thus allowing the use of the harmonic approximation. In this case, we replace the interaction term  $H^{\text{ME}}$  in Eq. (11) by

$$\hat{H}^{\text{ME}} = \hat{K}(s)\hat{\Phi}(\mathbf{Z}) = \hat{K}(s)\sum_{\xi}\hbar\gamma_{\xi}\hat{Z}_{\xi}, \quad (29)$$

where  $s$  denotes the system coordinates,  $\gamma_{\xi}$  denote the system-environment coupling constants and  $\hat{\mathbf{Z}} = \{\hat{Z}_{\xi}\}$  denotes the environment normal mode coordinates. For simplicity, we have assumed that  $H^{\text{ME}}$  contains a single term and have dropped the index  $u$ . Note that since  $\langle Z_{\xi} \rangle_{\text{R}} = 0$ , the expression for  $C_{uv}$  in Eq. (14) reduces to the two-point correlation function of the bath operator.

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Thus, we have for  $C_{uv}(t) = C(t)$

$$C(t) = \int_0^\infty d\omega \left( \cos(\omega t) \coth\left(\frac{\hbar\omega}{2k_B T}\right) - i \sin(\omega t) \right) \omega^2 J(\omega), \quad (30)$$

where  $J(\omega)$  is the spectral density,

$$J(\omega) = \sum_{\xi} g_{\xi}^2 \delta(\omega_{\xi} - \omega). \quad (31)$$

Some typical spectral densities are, cf. Ref. 12,  $\omega^2 J(\omega) = \theta(\omega) j_0 \omega^p e^{-\omega/\omega_c}$  or  $\omega^2 J(\omega) = \theta(\omega) \frac{j_0 \omega}{\omega^2 + \omega_D}$ .